Title
Sulfur dioxide and dimethyl sulfide in marine air at Cape Grim, 41 o S

Permalink
https://escholarship.org/uc/item/56b262nd

Journal
Tellus, 49B

Authors
Saltzman, ES
Ayers, GP
Cainey, JM
et al.

Publication Date
1997

License
CC BY 4.0

Peer reviewed
Sulfur dioxide and dimethyl sulfide in marine air at Cape Grim, Tasmania

By G. P. AYERS1,*, J. M. CAINEY1,2, R. W. GILLET1, E. S. SALTZMAN3 and M. HOOPER2
1Division of Atmospheric Research, CSIRO, Aspendale, Victoria 3195, Australia; 2Department of Applied Science, Monash University, Churchill, Victoria 3842, Australia; 3Division of Marine and Atmospheric Chemistry, University of Miami, Florida, FL 33149–1098, USA

(Manuscript received 6 September 1996; in final form 27 January 1997)

ABSTRACT

Results from one long-term study and one summer-time field campaign in which the sulfur dioxide (SO2) mixing ratio was determined in mid-to-high latitude marine air at Cape Grim, Tasmania, are presented and analysed to provide a perspective on the potential role of SO2 in the production of aerosol sulfate at this site. Sulfur dioxide at Cape Grim has a distinct seasonal cycle, with a maximum mixing ratio in summer and minimum in winter, consistent with a similar cycle observed previously at Cape Grim for dimethyl sulfide (CH3SCH3; DMS) and its other oxidation products. Concentrations of SO2 in the summer were typically 10 ppt (pmole mole\(^{-1}\)), which is considerably lower than those found at other sites subject to marine air more equatorial in origin. A modelling study suggests that differences between equatorial and mid-to-high latitude marine SO2 concentrations result from lower levels of the DMS precursor at mid latitudes and a lower rate of SO2 production at lower temperatures. The analysis also suggests the existence of an additional non-DMS source of boundary layer sulfur, relatively more important in winter when DMS levels are low. Entrainment from the lower free troposphere appears to be one likely source.

1. Introduction

The potential role of the marine atmospheric sulfur cycle in the regulation of the global climate has been much discussed following the hypothesis of Charlson et al. (1987). It is now accepted that gaseous dimethylsulfide (CH3SCH3; DMS) enters the marine atmosphere from the ocean as the result of biological processes, and that once in the atmosphere DMS undergoes a number of photochemical reactions, with major end products including aerosol sulfate and methanesulfonic acid (see the collection of papers edited by Restelli and Angeletti, 1993). One of the more stable intermediates in the oxidation process is sulfur dioxide (SO2), which can be converted into sulfate aerosol by both homogeneous gas-phase processes, and by heterogeneous processes (in cloud droplets or deliquesced salt particles; Sievering et al., 1995).

The importance of sulfur dioxide as an intermediate in the formation of sulfate has been subject to speculation, with some authors suggesting that sulfur trioxide (SO3) plays a more important role under cool, mid-to-high latitude conditions, but that SO2 is formed with high efficiency in warm tropical conditions (Bandy et al., 1992; Berresheim et al., 1995; Bandy et al., 1996). This is consistent with high latitude/Antarctic measurements of SO2 showing levels of only a few ppt, but considerably greater levels reported for the equatorial Pacific by Bates et al. (1993) during the SAGA3 cruises, where SO2 averaged 25 ppt, and by Bandy et al. (1996) who
reported an average of about 40 ppt from Christmas Island in July 1994. The latter data also concur with previous data from Amsterdam Island (latitude 38° in the southern Indian Ocean) where the equatorial air masses, which were sampled relatively frequently, exhibited SO₂ levels of about 40 ppt in midsummer, dropping to about 5 ppt in midwinter, at which time the local DMS mixing ratio was also much reduced (Putaud et al., 1992).

The Australian baseline station at Cape Grim, Tasmania (41°S) is located at similar latitude to Amsterdam Island, but provides an interesting contrast because Cape Grim samples air from the mid-to-high latitudes of the Southern Ocean, rather than from equatorial regions. This is because stringent local sampling conditions are employed to ensure that sampled air has no recent contact with the Australian continent, and anthropogenic emissions, which generally restricts air masses sampled to those having an origin at latitudes between 40° to 50° or even 60°S (Ayers and Gras, 1983; Ayers et al., 1996a). If the hypothesis discussed by Bandy et al. (1996) is correct, that high temperatures favour efficient SO₂ formation from DMS oxidation by OH, the corollary should be that at a site such as Cape Grim (where air mass origin is from mid-high latitude regions where temperature is low), the SO₂ yield from DMS oxidation and resultant atmospheric SO₂ level should also be low. In other words, this hypothesis would predict SO₂ levels at Cape Grim more akin to the few ppt previously reported for Antarctic waters than to the tens of ppt reported for Amsterdam Island and tropical marine locations. Here we explore this prediction by reporting data on SO₂ mixing ratios recorded at Cape Grim between 1990 and 1994.

2. Site

Cape Grim Baseline Air Pollution Station is situated on the remote north-west coast of Tasmania (40°40'56''S, 114°41'18''E), at the top of 90 m sheer cliffs, with a westerly aspect. Baseline air (i.e. clean, marine air) is that which originates from the remote Southern Ocean and arrives at the station in the sector 190° to 280°. Baseline air is encountered about 30% of the time, with sampling equipment employed in this work switched to operate only when baseline conditions occurred. The criteria employed were local wind direction between 190° and 280° and CN (condensation nucleus) count below 600 cm⁻³.

3. Methods

Between October 1990 and March 1993 SO₂ was determined in weekly-averaged samples using a slightly modified form of the carbonate-impregnated filter method described by Ferek et al. (1991). The modifications involved (i) use of 47 mm diameter filter substrates, (ii) an impaction stage upstream of the prefilter to remove alkaline salt particles prior to the triple filter pack, (iii) a Fluoropore 1 μm pore size prefilter instead of a Ze fluor filter, and (iv) a Millapore cellulose nutrient pad instead of Whatman 54 collection filters. Tests in ambient air at CSIRO, Aspendale indicated 100% collection SO₂ efficiency for the nutrient pads at ambient levels near 500 ppt. Like Ferek et al. (1991) we also paid particular attention to filter cleaning by leaching prior to use, utilisation of highest purity reagents for filter impregnation, and clean filter handling techniques in which all preparative work was carried out in a glove bag under dry, SO₂-free nitrogen.

Filterpacks were deployed for 1-week periods in parallel with an aerosol sampling program discussed previously (Ayers et al., 1991). The sampler was switched to operate only in clean marine air masses, as noted above. Flow rate employed was 30 litres per minute, providing weekly sample collection volumes that depended on the frequency of baseline conditions in each week. In acknowledgment of the low values of SO₂ anticipated and the difficulty of SO₂ determination at very low levels a criterion of 100 m³ was set as a minimum acceptable sample volume. If this amount of baseline air was not achieved in a given week, the sample was retained for a second week. By this means an average sample volume of 157 m³ was achieved, with the samples comprising a mixture of weekly and bi-weekly samples.

After exposure the filter pack was removed, capped and returned to CSIRO, where the filters were removed and stored at -20°C for periods ranging from one to several weeks before analysis, at which time the samples were extracted in 5 ml Milli-Q water, with 50 μl of chloroform added as
a bactericide. Laboratory tests indicated no change in recovered sulfate during filter storage. The extract was analysed using suppressed ion chromatography and a Dionex AS4A separation column, as outlined by Ferek et al. (1991).

At regular intervals during the experimental period field blanks were exposed, whereby the sampler was loaded as normal but the pump was switched on for 1 minute only. Taking a hypothetical sample volume of 157 m³, the mean and standard deviation of the sulfate levels derived from the 14 blanks corresponded to 0.64 ppt and 0.78 ppt, respectively. All data discussed later have been corrected downwards by the mean blank value.

In order to gain some perspective on the reliability of the impregnated filter method a separate SO₂ measurement study was carried out in November 1994, employing a completely different SO₂ measurement method, the HPLC-fluorescence method of Saltzman et al. (1993). In this method, ambient air was drawn through an inlet heated to 60°C, that contained a PTFE filter to remove sea salt particles. The air sample was then dried by passing through a Nafion drier, before entering a reaction coil, where the air was scrubbed with 10 µmolar formaldehyde solution and 0.84 mmolar disodium-EDTA to produce an aqueous solution of sulfite/bisulfite. Subsequent reaction with ortho-phthalaldehyde, in the presence of excess ethanolamine, yields a fluorescent isoindole, that was determined by HPLC separation on a 15 cm C-18 Spherosorb HPLC column, with fluorescence detection (Saltzman et al., 1993). Reagents were prepared daily and the system was also shut down daily and flushed with a methanol:water mix (80:20 by volume).

The typical daily sampling programme consisted calibration checks in the early morning and late afternoon followed by measurement of 10 ambient samples, 5 blanks, and a three point calibration which was designed to cover the range of ambient measurements. Gas phase standards were produced using an SO₂ permeation tube (Dynacal, 11.9 ng min⁻¹ at 303K) and a two-stage gas dilution system incorporating four mass flow controllers (Gallagher et al., 1996). The permeation tube was kept at 30°C and was subjected throughout the field work to a constant flow of high purity dry nitrogen. Blanks were produced by passing the permeation tube standards or ambient air through carbonate-impregnated filters. A typical blank response was equivalent to 4 ppt of SO₂ with variance (1σ) across a series of blanks at about half this level. Results were produced in real time (typically 6 samples per hour) yielding a continuous time series of SO₂ mixing ratio in both baseline and non-baseline conditions. Under baseline conditions the ambient SO₂ mixing levels were always close to, and at times were indistinguishable from the blank values.

Finally, aerosol methanesulfonate (MSA) data and atmospheric DMS data for the period October 1990 to March 1993 were taken from routine Cape Grim measurements, according to methods previously described (Ayers et al., 1991; Ayers et al., 1995). Note that the aerosol MSA data discussed later are total aerosol MSA loadings, derived from the sum of the fine plus course fraction samples described by Ayers et al. (1991).

4. Results

The SO₂ mixing ratios determined in weekly/bi-weekly samples between late 1990 and early 1993 are shown in Fig. 1. A seasonal cycle can be seen clearly, from an SO₂ maximum averaging about 10 ppt in mid-summer to a low of 2 ppt in mid-winter. Fig. 2 contains comparable DMS data from Cape Grim comprising approximately one

![Fig. 1. Time series of weekly/bi-weekly average SO₂ mixing ratios in baseline air at Cape Grim, 1990–1993.](image-url)
sample per week, which were presented and discussed by Ayers et al. (1995). The correspondence between the two series is obvious, in particular the pattern of interannual variability in peak summer concentrations is identical. The monthly mean values from both series are plotted in Fig. 3, where a consistent seasonal pattern is the major feature.

Fig. 2. Time series of 1-h average DMS mixing ratios, taken weekly in baseline air at Cape Grim, 1990–1993 (Ayers et al., 1995; copyright Journal of Geophysical Research).

The results from the HPLC measurements done in late spring/early summer in 1994 are shown in Fig. 4, in which the SO$_2$ data were averaged to hourly means. SO$_2$ mixing ratios are plotted together with the corresponding condensation nucleus (CN) data. The large peaks in both series correspond to periods when the station received continental air masses from either the populated regions of the Australian mainland to the North, or from the island of Tasmania. The hours of low and relatively constant CN count (<1000 cm$^{-3}$) correspond to periods when the station received marine air masses from the remote Southern Ocean. In these baseline air masses the sulfur dioxide levels were extremely low, as shown in Fig. 4, often near or below the detection limit of ~3 ppt with only an occasional value exceeding 10 ppt. The grand average baseline SO$_2$ level over the experimental period (includes all data, even when blank exceed sample value yielding a small negative value) was 4 ± 5 (1 σ) ppt.

5. Discussion

The average value of 4 ± 5 ppt for SO$_2$ mixing ratio determined in November 1994 using the HPLC fluorescence method is not statistically different from the mean value of 8 ± 6 ppt (1 σ) determined from the 1990–1993 weekly filter-based samples taken at the same time of year. This consistency between measurements made
with different methods is important. It adds considerable confidence to the discussion, since the Cape Grim SO$_2$ values are very low, and obtaining verifiable results at low levels has been a problem in the past (see CITE 3, Bates et al., 1993).

The very low SO$_2$ values found and the evident coherence between the SO$_2$ annual cycle and the DMS annual cycle shown in Fig. 3 provides strong prima facie evidence that in marine air at Cape Grim DMS oxidation is a primary source of boundary layer SO$_2$. Such a seasonal coherence has been noted previously only for Amsterdam Island, in the southern Indian Ocean (Putaud et al., 1992).

The summer-time SO$_2$ to DMS ratio in the Cape Grim data is approximately 0.1, about half the value of 0.2 reported by Putaud et al. (1992) for Amsterdam Island and the value of 0.2–0.3 evident in the equatorial Christmas Island data of Bandy et al. (1996). This trend towards lower SO$_2$ to DMS ratio in samples from higher latitudes is consistent with the hypothesis discussed in detail by Bresheir et al. (1995) and adopted by Bandy et al. (1996), that predicts lower SO$_2$ yields from DMS oxidation by hydroxyl (OH) at lower temperatures. This hypothesis is predicated on the argument that initial OH attack on DMS occurs by either OH abstraction of a hydrogen atom, or addition of OH to the sulfur atom. Abstraction is favoured at higher temperatures and, according to Bandy et al. (1996), leads to SO$_2$, whereas the addition pathway that is presumed to lead to MSA and SO$_3$ formation becomes more favoured at lower temperatures.

The clearly decreasing trend in absolute SO$_2$ level and in SO$_2$/DMS ratio going from Christmas Island and Amsterdam Island to Cape Grim appears supportive of this argument that lower temperature results in relatively less SO$_2$ production. However the situation must be more complicated than this, since a similar effect would be anticipated in seasonal data from any single site when moving from summer to winter: an increase in MSA/DMS ratio and decrease in SO$_2$/DMS ratio would be predicted at the lower wintertime temperature. In fact, as shown in Fig. 5, the opposite trends are evident in the data from Cape Grim.

Although the seasonal decrease rather than increase in the MSA/DMS ratio and increase rather than decrease in SO$_2$/DMS in winter are inconsistent with the hypothesis outlined above, these patterns are consistent with the similar observation that the aerosol MSA/nss-SO$_4^{2-}$ ratio decreases in winter (Ayers et al., 1991).

The inconsistency between the apparent temperature dependence of the DMS oxidation product ratios when temperature change is seasonally induced, rather than latitudinal in origin, suggests the need to consider temperature dependencies in reactions other than the initial attack on DMS by OH. Moreover, as suggested by the work of Koga and Tanaka (1993) seasonal dependencies in other oxidising species such as NO$_3$ radical and perhaps ozone may influence significantly the rates of a number of the intermediate reaction pathways in the complex DMS oxidation change.

A perspective on the importance of these complexities can be gained by attempting to model the Cape Grim annual SO$_2$ cycle using the large and comprehensive reaction scheme of Yin et al. (1990), as modified by Ayers et al. (1996b). The modifications centre on inclusion of temperature dependent rates for the key CH$_3$SO$_2$ and CH$_3$SO$_3$ decomposition pathways that in the Yin et al. (1990) scheme determine the final ratios of MSA, SO$_2$ and nss-SO$_4^{2-}$ formation. This scheme was employed in a boundary layer box model, using appropriate seasonally varying boundary conditions of temperature, humidity, boundary layer height, and reagent gas (CO, CH$_4$, O$_3$ and NO$_x$) concentrations, as discussed in detail by Ayers et al. (1996b). The annual cycle was approximated.
by modelling the middle day of each month, with oceanic DMS fluxes adjusted slightly from the multi-year mean values of Ayers et al. (1995) so as to give model DMS mixing ratios equal to the specific monthly mean DMS values shown in Fig. 3.

Fig. 6 contains a plot of modelled MSA/DMS and SO₂/DMS mole ratios, which may be compared with the measured values shown in Fig. 5. Fig. 7 contains a comparison of observed and modelled SO₂ seasonal cycles. The comparison between Figs. 5 and 6 indicates that the modelled MSA/DMS ratio reproduces the general feature of a summer maximum/winter minimum evident in the data, however the SO₂/DMS ratio does not reproduce the observed summer minimum/winter maximum, while at the same time the modelled SO₂ mixing ratio is too low in absolute terms (Fig. 7): the model suggests about 15% of sulfur from DMS oxidation passes through SO₂.

A possible explanation for the discrepancy in the case of SO₂ is that another source of SO₂ exists at Cape Grim, a suggestion consistent with an earlier suggestion of a similar nature made with regard to submicrometre aerosol non-sea salt sulfate (Ayers et al., 1991). One possible source of additional SO₂ (and sulfate) is oxidation of other trace gases such as hydrogen sulfide, methyl mercaptan, dimethyl disulfide and carbonyl sulfide. However no measurements of these species have been undertaken at Cape Grim, so this possibility cannot be taken further here. A second possibility is that SO₂ is entrained from the lower free troposphere, a process hypothesised by Raes (1995) as a key source of condensation nuclei and cloud condensation nuclei in the marine boundary layer. Entrainment has been shown to be involved in maintenance of marine boundary layer ozone levels at Cape Grim (Ayers and Galbally, 1995; Ayers et al., 1996a), and has also been invoked in recent explanations of observed patterns in sulfur gas and aerosol species measured in equatorial marine air at Christmas Island (Huebert et al., 1996; Clarke et al., 1996). Thus entrainment may provide a source (at least in part) of the additional SO₂ that would be required to bring the modelled and observed levels at Cape Grim into agreement. The amount of additional SO₂ required is modest, as shown in both Figs. 6 and 7 where the SO₂/DMS ratio and absolute SO₂ levels reproduce rather well the observed values if a constant 3 ppt of additional SO₂ is added throughout the year.

6. Summary and conclusions

Measurements of marine boundary layer SO₂ mixing ratio at Cape Grim show levels signific-
antily lower than those observed elsewhere at lower latitudes, consistent with recent hypotheses that SO$_2$ production from DMS oxidation is less efficient at lower temperatures. The observed SO$_2$ levels at Cape Grim followed the observed seasonal cycle in DMS, with SO$_2$ averaging 10 ppt in mid-summer and 2 ppt in mid-winter.

Model predictions of the MSA/DMS ratio reproduced reasonably well the summer maximum/winter minimum in this ratio observed at Cape Grim, however the modelled SO$_2$/DMS ratio lacked the observed summer minimum/winter maximum and the modelled absolute SO$_2$ levels were below those observed. This discrepancy is removed if another non-DMS source of SO$_2$ is hypothesised, at the modest level of about 3 ppt throughout the year. Possible origins of this small amount of additional SO$_2$ might include oxidation of other reduced sulfur gases and entrainment from the lower free troposphere.

Additional measurement programs at Cape Grim will be required for these possibilities to be assessed. Moreover, the SO$_2$ data reported here were taken using methods operating at the limit of performance of these methods, yielding observations at undeniably low levels, but of limited precision. Detection limits must be improved at least an order of magnitude if time series data on baseline SO$_2$ levels are to provide any information on daytime photochemical production rates and night-time heterogenous loss rates.

7. Acknowledgement

This work rests in large part on the careful, skilful and dedicated efforts of many Cape Grim staff over many years, without whose enthusiastic assistance the measurement program could not have been undertaken. The Cape Grim program is funded by the Commonwealth of Australia, and is administered jointly by the Bureau of Meteorology and CSIRO. The work was also supported in part by the US National Science Foundation under grant ATM-9420157. JMC gratefully acknowledges a Monash University Overseas Study Grant.

REFERENCES


